

D7

R01K/606



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number : **0 609 994 A1**

(12)

EUROPEAN PATENT APPLICATION

(21) Application number : **94300355.8**

(51) Int. Cl.⁵ : **D21H 19/54, C08L 3/08**

(22) Date of filing : **19.01.94**

(30) Priority : **30.01.93 GB 9301896**

(43) Date of publication of application :
10.08.94 Bulletin 94/32

(84) Designated Contracting States :
AT BE CH DE DK ES FR GB GR IE IT LI NL PT SE

(72) Inventor : **Bergh, Niels-Olaf, Dr.**
Lustraetenweg 25
D-47802 Krefeld (DE)
Inventor : **Hemmes, Jan-Luiken, Dr.**
Wilhelmshofallee 63
D-47799 Krefeld (DE)
Inventor : **Olander, Lars**
Dalgangen 14
S-13900 Varmdo (SE)

(71) Applicant : **CERESTAR HOLDING BV**
Nijverheidsstraat 1
P.O. Box 9
NL-4550 AA Sas Van Gent (NL)

(74) Representative : **Wilkinson, Stephen John et al.**
Stevens, Hewlett & Perkins
1 St. Augustine's Place
Bristol BS1 4UD (GB)

(54) **Starch composition.**

(57) A composition which is useful as a binder in paper coating colours which comprises either a cationic starch and/or a cationic synthetic polymer in combination with a starch containing at least one non-ionic substituent or a cationic starch containing at least one non-ionic substituent. Preferably the binder is a mixture of a cationic starch and a hydroxyalkyl starch.

EP 0 609 994 A1

BEST AVAILABLE COPY

The present invention relates to starch compositions, in particular to a starch composition for use as a binder in coating colours and to coating colours thereby produced. The invention also relates to paper coating processes using such coating colours.

The manufacture of paper customarily includes a process step in which the base paper is coated on one or both sides by pigment designed to change the appearance of the paper by improving its opacity and imparting a smooth and receptive surface for printing or for an additional coating step. The pigment coating is applied to the base paper in the form of a water-suspension, called a "coating colour", which contains as essential ingredients a pigment and binder. The suspension generally contains 35 to 70% total solids and after application the coating must be dried by removal of water from the film.

The pigment usually makes up 50 to 90% of the dry solids of the coating colour and has the function of forming on the paper surface a smooth, level, ink-receptive printing layer. To this end the pigment particles are of such a size that they can fill in the spaces between fibres on the paper surface and thereby form a more nearly uniform surface mat. Kaolin clays are widely used pigments as are talc, titanium dioxide and calcium carbonate, the choice of pigment being dictated by the properties required for the paper surface eg. high gloss, high dye receptivity and increased printability.

The function of the binder is to bind the pigment particles together and, in turn, the coating layer to the paper surface. The strength of the bond must be such that the coating layer is not detached ("picked") by tacky printing inks. The binder also has an influence on other properties of the coating layer and increasing quantities of binder can affect the brightness, gloss and printability of the latter. Usually, the amount of binder in coating colour is 5% to 25% by weight based on pigment but, exceptionally, higher amounts may be used. Commonly used binders include starches and certain synthetic polymers eg dispersions of styrene-butadiene or styrene-acrylate copolymers or polyvinyl alcohol. The present invention however is mainly directed at coating colours in which the binder is partly or entirely derived from starch.

Unmodified starches are not suitable as binders because when used in the concentration necessary for effective bonding the coating colour is too viscous. It is common practice therefore to use modified starches as binders. Modification may take place by acid, enzymatic or thermochemical treatment whereby the starch is degraded and its molecular weight is decreased. Alternatively, the starch may be oxidised eg. with hypochlorite which produces a product giving an aqueous solution which is clear and much more fluid at high concentration than is the parent starch. Substituted starches comprising, for example, a hydroxyethyl substituent may also be used and have the advantage that the presence of the substituent inhibits the undesirable gelling or retrogradation of the starch when its hot aqueous solution is cooled.

Various methods are available for applying the coating colour to the paper surface differing mainly in the means adopted for metering the coating onto the surface so as to obtain a controlled and even coating thickness. In the "film-press" method of application the paper is fed through the nip between two cooperating feed rollers, coating colour applied to one or both rollers being transferred to one or both sides of the paper under pressure so as to effect a compressed coating on one or both surfaces of the paper as desired. The thickness of the coating colour layer on the feed roller(s) is important since it controls the thickness of the layer applied to the paper. The "pre-dosing" of the coating colour onto the feed roller may be achieved by feeding the colour into the nip between the roller and an adjacent bent blade or rotating smooth rod. The hydrodynamic pressure which is generated in the nip between the roller and blade or smooth rod forces the coating colour through the nip onto the feed roller and, in general, the higher the hydrodynamic pressure the thicker the coating applied to the feed roller.

The hydrodynamic pressure developed in the coating colour is dependant inter alia upon the solids content of the coating colour and the viscosity of the latter at the time of application. The two pre-dosing methods described above require different hydrodynamic pressures and, it is preferred to have a higher hydrodynamic pressure when the coating colour is applied by a smooth rod than it is when using a bent blade. We have now found that to provide a starch-based binder having the desired rheology for film-press coating in general and for smooth rod pre-dosing in particular it is advantageous to use a combination of modified starches or a combination of a modified starch and a synthetic polymer or to use a single starch in which the starch has been modified in two different ways.

Accordingly, the invention comprises a composition which is useful as a binder in coating colours and which is characterised by the presence of

- (a) a cationic starch and/or a cationic synthetic polymer in combination with a starch containing at least one non-ionic substituent or,
- (b) a cationic starch containing at least one non-ionic substituent.

U.S. patent 3 598 623 describes the use of carboxyl starch amine ethers as binders for paper coating colours. Such starches contain both an anionic group and a cationic group and may be made by cationising an oxidised starch whereby a tertiary amine or quaternary ammonium group is introduced into a starch already

containing a carboxyl group. We have found however that the COD (chemical oxygen demand) is higher for starch ethers of the US patent than for the compositions of the present invention, which is an important factor in the paper industry with respect to effluent disposal. In addition, we have found that physical mixtures of a cationic starch and an oxidised starch are, unlike the compositions of the present invention, unstable after ge-

latinisation.

The cationic synthetic polymer may be a low molecular weight highly substituted synthetic polymer with high charge density eg polyethyleneimine, but preferably the cationic component is a cationic starch, more preferably a cationic starch in which the cationic substituent is a tertiary amino or quaternary ammonium group, particularly the latter eg. the product obtained by reacting maize, waxy-maize, tapioca, wheat, barley or potato starch with the chorhydrin, 3-chloro-2-(hydroxypropyl)-trialkyl ammonium chloride or its epoxide equivalent. "Alkyl" in the latter compound is suitably methyl, ethyl or propyl.

Preferably the non-ionic substituent in the compositions according to the present invention is an ester group as in a starch ester or a hydroxyalkyl group as in a hydroxyalkyl-substituted starch. Suitable starch esters for use in the composition according to the invention are short chain (C_1 to C_4) alkyl esters eg. starch acetate or starch propionate, particularly the former. A hydroxyalkyl substituted starch for use in the composition is preferably hydroxyethyl or hydroxypropyl starch, especially the latter. The cationic starch and the starch containing a non-ionic substituent are suitably the subject of a mild degradation treatment eg with acid, enzyme or thermally either before the starch is modified or, if after modification, either before or after the composition is prepared. Preferably, the degradation is achieved thermally in the presence of a thermochemical conversion agent such as potassium persulphate.

It is also possible to obtain the objects of the invention by combining the cationic function and the non-ionic function in the one and the same starch molecule by means of a double modification of the starch eg by cationising a starch containing a non-ionic, eg hydroxypropyl substituent.

The preferred weight ratio of cationic starch to the starch containing a non-ionic substituent is 10 to 60 : 90 to 40 preferably 30 to 50 : 70 to 50. The preferred composition is 30 to 50 parts by weight of a cationic starch which is the product of reacting 3-chloro-2 (hydroxypropyl)- trimethyl ammonium chloride with maize or potato starch together with 70 to 50 parts by weight hydroxypropyl starch (maize or wheat)

The invention also comprises a coating colour which comprises an aqueous suspension of one or more pigments and a binder as hereinbefore described. The coating colour preferably comprises 1 to 50 parts by weight, more preferably 10 to 25 parts, by weight, binder per 100 parts by weight pigment. The mixture may also contain other additives eg latex suitably in an amount 1 to 50 parts by weight per 100 parts by weight pigment preferably 1 to 10 parts by weight.

The invention also comprises a process for applying a coating colour to a paper base by a film-press method in which the coating colour is that described above. The coating colour preferably contains 25 to 75% by weight solids, more preferably about 50% by weight solids.

The invention will now be further illustrated by reference to the following Examples.

Examples

A number of coating colour formulations were prepared by blending cooked starch dispersions containing 20 to 22% by weight solids and a predispersed pigment slurry containing 75% by weight solids.

The starch dispersions were in turn prepared by heating a slurry of the relevant starches in a continuous cooker at 130 to 140°C in the presence of varying amounts of a thermochemical conversion agent, SP26, a commercially available blend of potassium persulphate and buffering chemicals.

The coating colour formulations contained 15 parts by weight total starch and 5 parts by weight latex calculated as dry product on 100 parts by weight dry pigment Hydrocarb 70 (a calcium carbonate ie. chalk coating pigment)

The coating colour formulations were evaluated in a pilot scale film-press coater provided with a smooth rod as the predosing means. The rod was operated at a constant pressure of 1×10^5 Pa and the quantity of the composition deposited on the woodfree coating base paper was determined gravimetrically by means of a doctor knife of specified width being applied to the film-press roll, the coating which was scraped off in a set period of time being weighed.

The followed Table contains the compositions of the various formulations tested and the relationship between the Brookfield viscosities of the formulations (measured at 30°C and 100 rpm) and the weight of the coating applied to the paper roll.

	Starch Components	Amount of SP26	Starch + Viscosity	D.S. of Coating** Colour Composition	Viscosity of ++ Coating Colour Composition	Coating++ wt(g)
5	A*	0.80	250	52	280	2.0
	A	0.65	400	52.4	460	6.5
	A	0.50	1500	52.4	500	5.0
10	50 % A + 50% B	0.55	300	52.6	1260	9.0
	50 % A + 50% B*	0.35	390	51.9	980	7.0
	50 % A + 50% B	0.20	1100	50.2	2440	12.0
	70 % A + 30% B	0.70	220	52.7	660	10.5
	70 % A + 30% B	0.62	380	52.0	660	8.0
15	70 % A + 30% B	0.55	800	52.1	1280	12.5
	A	0.8	250	48.6	156	5.0
	A	0.65	400	48.7	180	6.0
	A	0.5	1500	48.3	200	2.5
	50 % A + 50% B	0.55	300	48.3	580	8.5
	50 % A + 50% B	0.35	390	48.7	675	7.0
20	50 % A + 50% B	0.20	1100	48.7	1840	11.5
	70 % A + 30% B	0.70	220	48.2	460	6.5
	70 % A + 30% B	0.55	800	48.6	720	8.0
	A	0.50	1500	56.8	960	5.0

* Starch A was a propoxylated maize starch

* Starch B was a cationic maize starch (cationisation reagent N-(3-chloro-2-hydroxypropyl)-N,N,N-trimethyl ammonium chloride)

** D.S. = dissolved solids

+ viscosity of 25% solids at 50°C

++ preferred coating weight 10 grams

Claims

1. A composition which is useful as a binder in coating colours which is characterised by the presence of
 - (a) a cationic starch and/or a cationic synthetic polymer in combination with a starch containing at least one non-ionic substituent or,
 - (b) a cationic starch containing at least one non-ionic substituent.
2. A composition according to claim 1 characterised in that the cationic component is a low molecular weight, highly substituted synthetic polymer with high charge density eg. polyethyleneimine or a cationic starch in which the cationic substituent is a tertiary amine or quaternary ammonium group.
3. A composition according to claim 2 characterised in that the cationic starch is the product obtained by reacting maize, waxy-maize, tapioca, wheat, barley or potato starch with a 3-chloro-2-(hydroxypropyl)-trialkyl ammonium chloride.
4. A composition according to any one of the preceding claims characterised in that the non-ionic substituent is an ester group as in a starch ester eg a C₁ to C₄ alkyl ester such as starch acetate or a hydroxyalkyl group as in a hydroxyalkyl substituted starch eg hydroxyethyl or hydroxypropyl starch.
5. A composition according to any one of the preceding claims characterised in that the cationic starch and the starch containing a non-ionic substituent are subjected to a mild degradation treatment eg. thermally in the presence of a thermochemical conversion agent or with an acid or enzyme.
6. A composition according to any one of the preceding claims characterised in that the weight ratio of the cationic starch to the starch containing a non-ionic substituent is 10 to 60 90 to 40 preferably 30 to 50 :

70 to 50.

- 5
7. A composition according to any one of the preceding claims characterised in that it comprises 70 to 50 parts by weight hydroxypropyl starch , together with 30 to 50 parts by weight of a cationic starch which is the product of reacting maize or potato starch with 3-chloro-2-(hydroxypropyl)-trimethyl ammonium chloride or its epoxide equivalent.
- 10
8. A coating colour characterised in that comprises an aqueous suspension of one or more pigments and a binder according to any one of the preceding claims, preferably 1 to 50 parts by weight, more preferably 10 to 25 parts by weight, binder per 100 parts by weight pigment.
- 15
9. A coating colour according to claim 8 characterised in that it also comprises latex preferably 1 to 50 parts by weight, more preferably 1 to 10 parts by weight, per 100 parts by weight pigment.
- 20
10. A process for applying a coating colour to a paper by a film-press method characterised in that the coating colour has a composition according to claim 8 or claim 9.
- 25
-
- 30
- 35
- 40
- 45
- 50
- 55



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 30 0355

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cls)
X	EP-A-0 350 668 (NATIONAL STARCH AND CHEMICAL CORPORATION) * page 2, line 35 - line 44 * * page 3, line 23 - line 36 * * page 4, line 6 - line 7 * * claims 1-5 *	1,2,4-6	D21H19/54 C08L3/08
X	DE-A-15 46 416 (NATIONAL STARCH AND CHEMICAL CORP.) * page 4, line 22 - page 5, line 11 * * page 13 * * claims *	1,2,4, 8-10	
X	US-A-3 052 561 (J. KRONFELD) * column 3, line 7 - line 16 * * examples * * claims *	1,2,4,5, 8	
D,A	US-A-3 598 623 (R. M. POWERS ET AL.) * example 1 *	1,3,8,10	TECHNICAL FIELDS SEARCHED (Int.Cl.5)
A	US-A-3 719 514 (TAYLOR) * column 2, line 54 - line 58 * * column 3, line 28 - line 56 * * column 4, line 54 - column 5, line 18 * * column 7, line 3 - line 10 * * examples *	1,2,8-10	C08L D21H
A	PATENT ABSTRACTS OF JAPAN vol. 14, no. 280 (C-729)(4223) 1990 & JP-A-28 004 598 (SUMITOMO CHEM. CO LTD) 26 March 1990 * abstract *	1,8,10	
A	US-A-3 988 522 (G. BERSTEIN) * example 2; table 3 *	1,8	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 18 April 1994	Examiner Mazet, J-F
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons * : member of the same patent family, corresponding document</p>			

EPO FORM 1500 (01/92) (Rev.01)